

Supporting Information

Water Assisted Formation of Highly Oriented CsPbI₂Br Perovskite Films with Solar Cell Efficiency Exceeding 16%

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Experimental Section

Chemicals:

Cesium iodide (CsI, 99.999%), lead iodide (PbI₂, 99.9%), lead bromide (PbBr₂, 99.9%), dimethyl sulfoxide (DMSO, 99.8%), isopropanol (IPA, anhydrous, >99.5%), titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, 99.95%), 4-tert-Butylpyridine (tBP, 96%) and chlorobenzene (CB, 99.9%) were purchased from Sigma-Aldrich. P3HT was purchased from Xi'an Polymer Light Technology Corp. Fluorine-doped tin oxide (FTO) substrates (8 Ω/sq) were purchased from Nippon Sheet Glass.

Device Fabrication:

FTO substrates were ultrasonically cleaned by detergent solution, distilled H₂O, alcohol, and acetone for 20 min respectively. After being dried by nitrogen flow, the FTO substrates were treated by an ultraviolet ozone cleaner for 15 min. TiO₂ precursor was prepared by dissolving 0.15 mol titanium diisopropoxide bis(acetylacetonate) in 1 mL ethanol. To obtain a compact TiO₂ layer, TiO₂ precursor was spin-coated on the substrate at 3000 rpm for 30 s, followed by thermal annealing at 500 °C for 30 min. The compact TiO₂ coated substrates were also treated by an ultraviolet ozone cleaner for 15 min before use. The H₂O/IPA solutions were prepared by adding distilled H₂O into IPA to the desired concentration. The perovskite precursor solution was prepared by dissolving 311.77 mg CsI, 276.61 mg PbI₂, 220.20 mg PbBr₂ in 1 mL DMSO, followed by stirring at 50 °C overnight in a nitrogen-filled glove box. The as-prepared CsPbI₂Br precursor was filtered by a 0.2 μm polytetrafluoroethylene filter to get the clear solution before use. Subsequently, 35 μL perovskite precursor were loaded onto the compact TiO₂ substrate and spin-coated via a three-step process, the first step is 500 rpm for 20 s, the second step is 3000 rpm for 30 s, and the third step is 6000 rpm for 15s, respectively. At about 55s during spin-coating, the IPA solution with different amount of H₂O was dropped

on the precursor films. Then, the films were transferred to the hotplate in 3 seconds and annealed immediately at 300 °C for 10 min in glove box. After cooling down to room temperature, P3HT transport layer was deposited by spin-coating at 4000 rpm for 30s and annealed on a hot plate at 120 °C for 10 min. A total of 1 mL of P3HT in CB solution contained 15 mg P3HT with the addition of 11.2 μ L tBP and 54 μ L Li-TFSI in acetonitrile (10 mg/mL). Finally, 100 nm Au was thermally deposited onto the transport layer under vacuum as the back contact.

Characterization:

Field emission scanning electron microscopy (FESEM, HITACHI S4800) and atomic force microscopy (AFM, Veeco/DI) were used to characterize the morphology and roughness of the CsPbI₂Br films. X-ray diffraction (XRD) patterns were recorded with an X-ray diffractometer Bruker D8 Advance operated Cu K α radiation. UV-vis spectra were collected using a Cary 500 UC-Vis-NIR spectrophotometer. Photoluminescence (PL) spectra was acquired at room temperature by exciting the samples deposited onto a non-conducting glass with the Fluorolog-3-p spectrophotometer under the excitation wavelength of 380 nm. Time-resolved PL experiments were performed by exciting the samples deposited onto glass substrates using the second harmonic of a picosecond mode-locked Ti-sapphire laser (80.5 MHz) at 420 nm under ambient conditions. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at the BL14B1 beamline of the Shanghai Synchrotron Radiation Facility with a grazing incidence angle of 0.2°. Both the surface and cross-section morphology measurements were performed with Hitachi S-4800 field-emission electron microscope. X-ray photoelectron spectroscopy (XPS, PHI5300, Mg anode, 250 W, 14 kV) was used to analyze the chemical states of the CsPbI₂Br precursor films, and the binding energy of the C 1s peak at 284.8 eV was taken as an internal reference. Ultraviolet photoelectron spectroscopy (UPS) spectra was recorded with He source of incident energy of 21.22 eV (He I

line) in Ningbo Institute of Industrial Technology, CAS, Ningbo. The Current density-Voltage (J-V) curves of the photovoltaic devices were measured using a Keithley 2400 digital sourcemeter with a scan rate of 0.15 V s^{-1} under a simulated AM 1.5G spectrum and a solar simulator (Solar IV-150A, Zolix). Before each measurement, light intensity was calibrated with a standard Newport calibrated KG5-filtered Si reference cell. The external quantum efficiency (EQE) spectra was measured by a Newport-74125 system, calibrated by Si reference solar cell. The steady state photocurrent output of the best-performing devices was measured by biasing the device at maxing power point by a Keithley 2400 digital sourcemeter. Devices were masked with a metal aperture to define the active area of 0.0625 cm^2 .

Supporting Figures and Tables

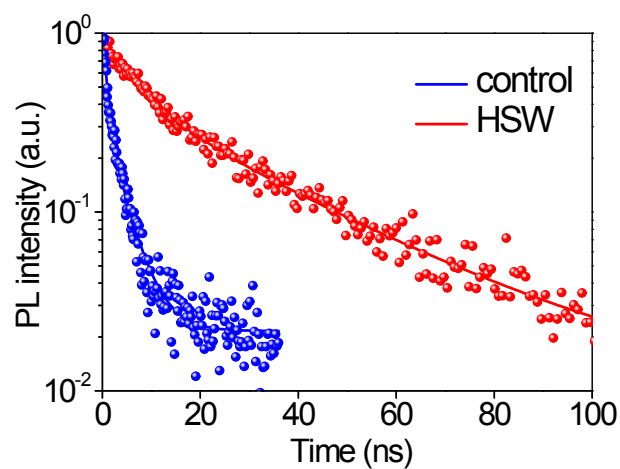


Figure S1. Time-resolved photoluminescence spectra (TRPL) decay curves of the CsPbI₂Br films on glass with and without HSW treatment. Isopropanol with 1.5 vol% of H₂O was used as the washing solvent.

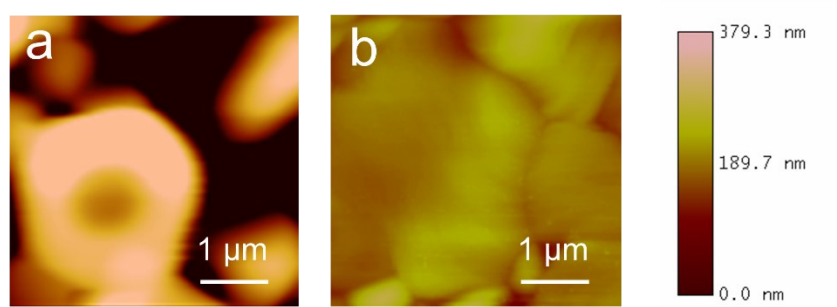


Figure S2. AFM images of CsPbI₂Br films obtained via (a) control and (b) HSW methods.

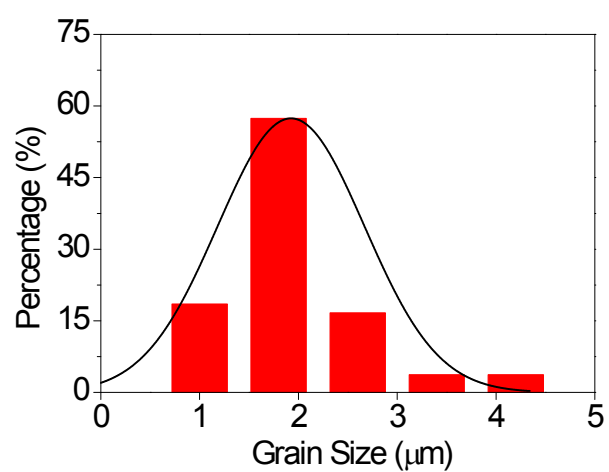


Figure S3. Statistical distribution of grain size for the CsPbI₂Br film prepared with HSW method. Isopropanol with 1.5 vol% of H₂O was used as the washing solvent.

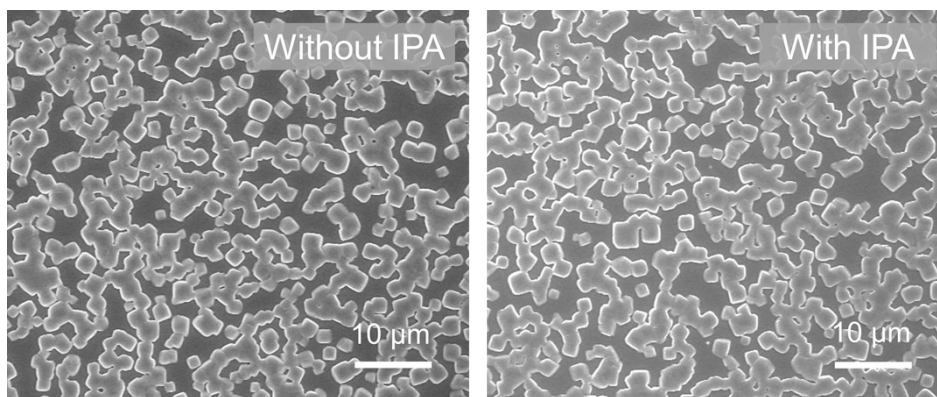


Figure S4. SEM image of CsPbI₂Br films prepared by one-step spin-coating with and without IPA washing.

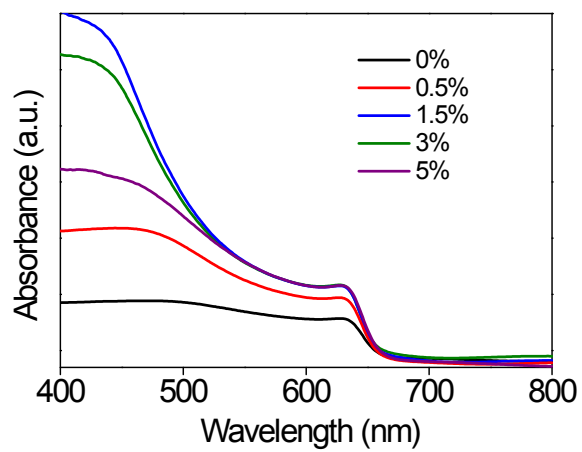


Figure S5. UV-vis absorption spectra of the CsPbI₂Br films prepared by HSW method with different concentrations of H₂O.

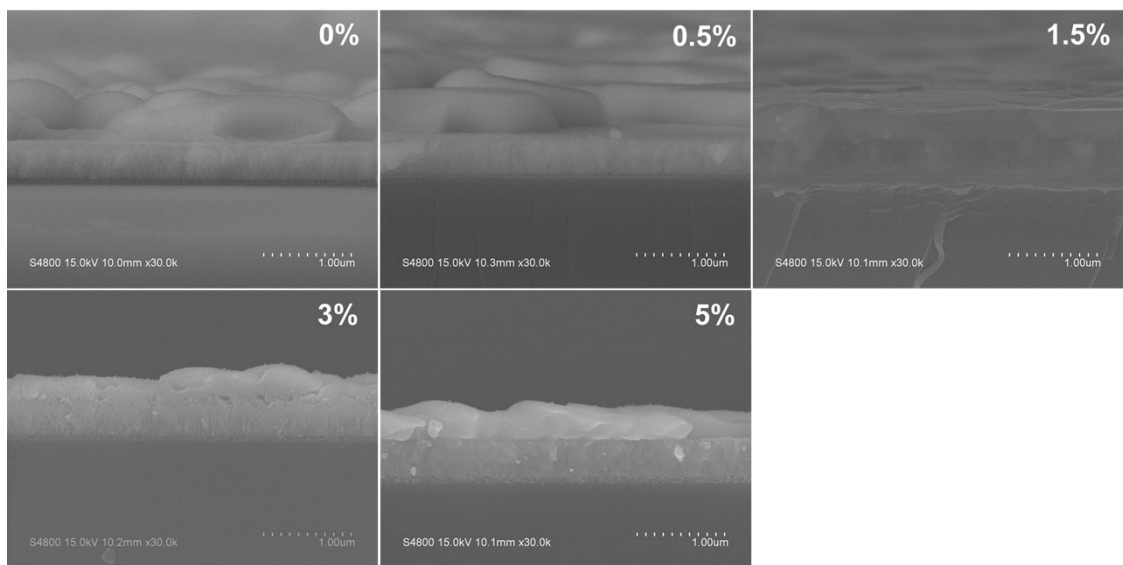


Figure S6. Cross-sectional SEM images of CsPbI₂Br films prepared by HSW method with different concentrations of H₂O.

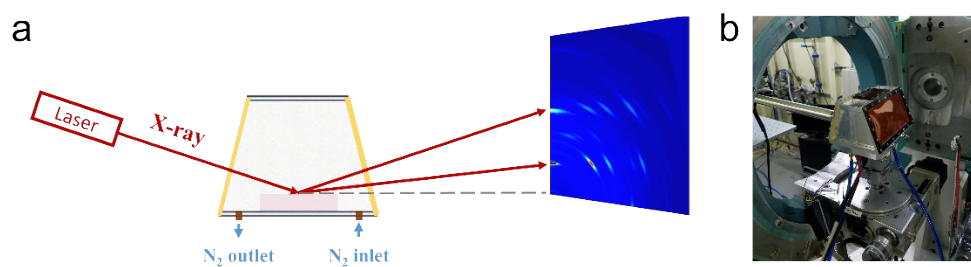


Figure S7. (a) Schematic and (b) photograph of the experimental setup for GIWAXS characterization.

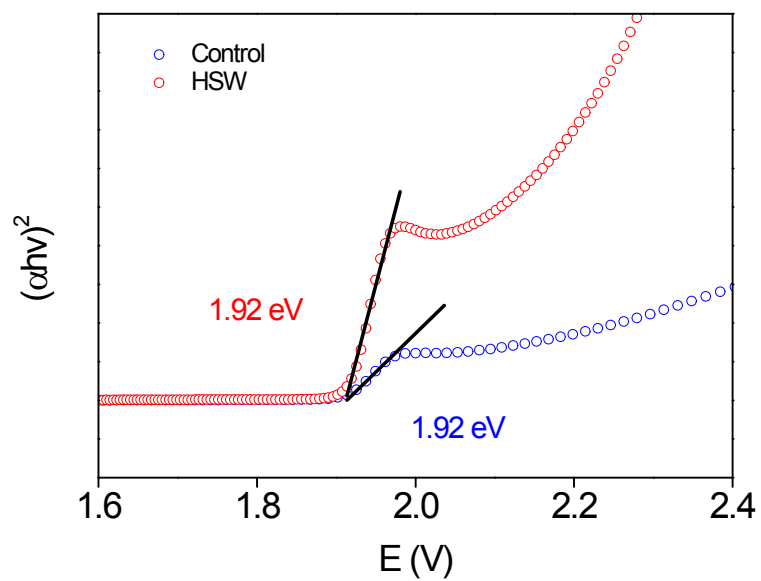


Figure S8. Tauc plots of control (blue) and HSW (red) CsPbI₂Br films.

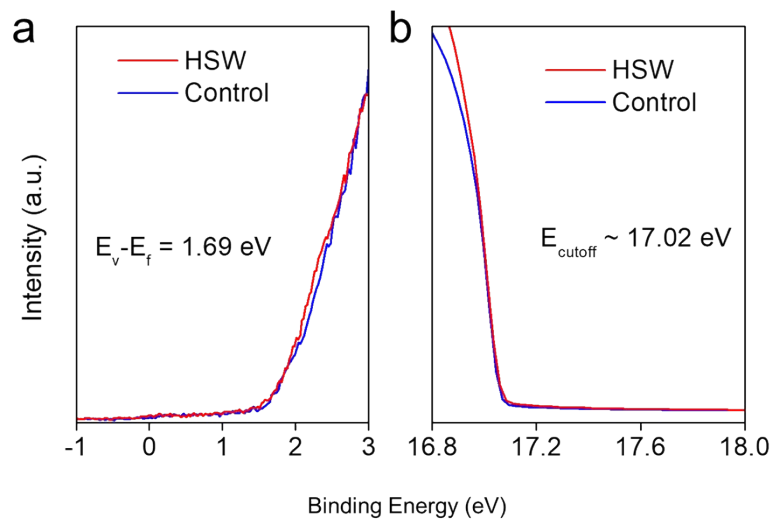


Figure S9. (a) Valence band edge and (b) secondary electron cutoff edge of the control and HSW CsPbI₂Br films.

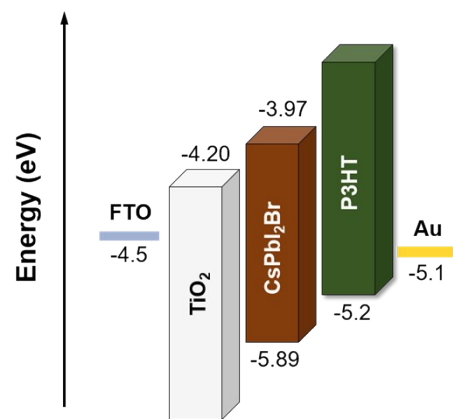


Figure S10. Energy band diagram of the as-prepared PSCs by using HSW CsPbI₂Br perovskite layer.

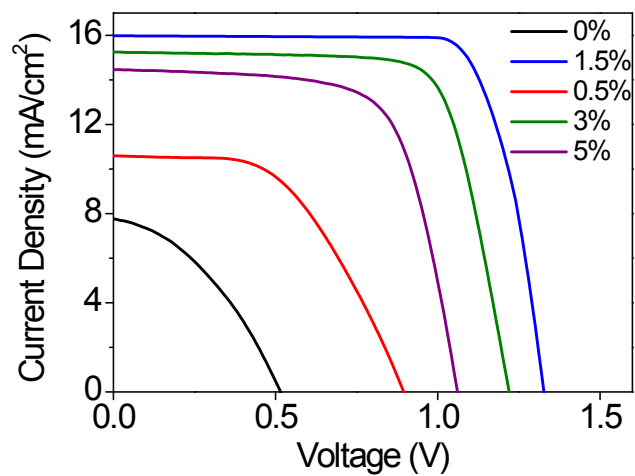


Figure S11. J-V curves of the champion devices fabricated by HSW method with different concentration of H₂O.

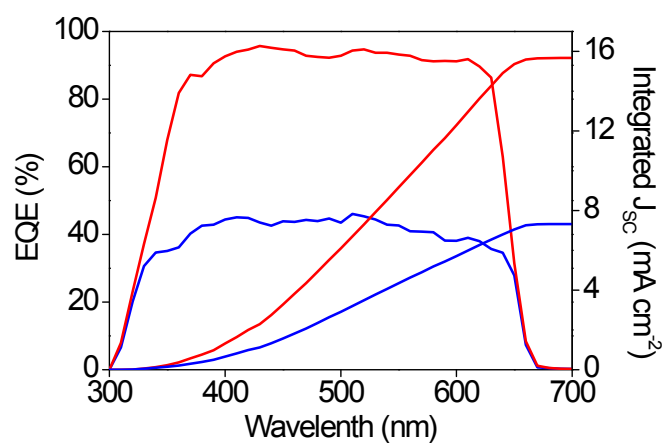


Figure S12. EQE spectra and integrated short-circuit current density of the control device (blue) and the HSW device (red).

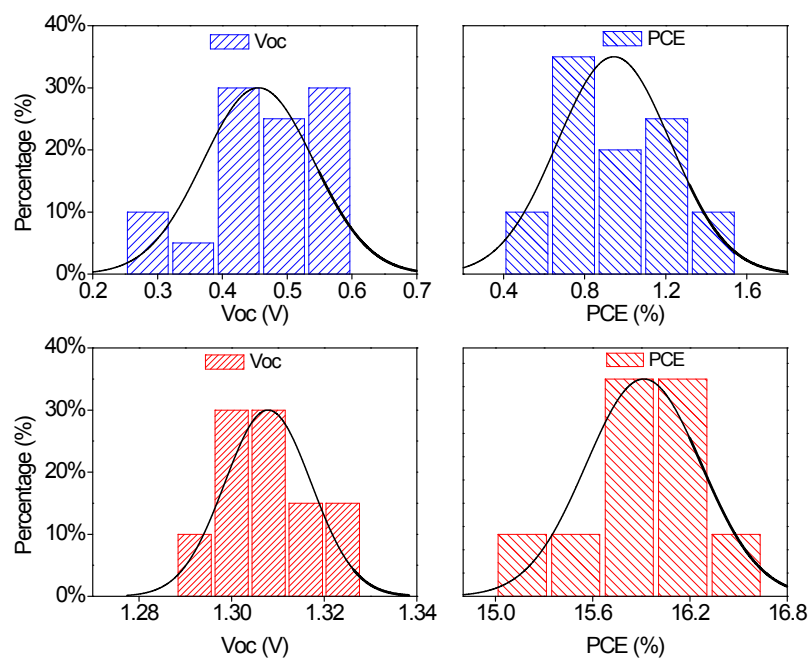


Figure S13. Statistics of V_{oc} and PCE distribution from 20 individual control (blue) and HSW (red) PSC devices.

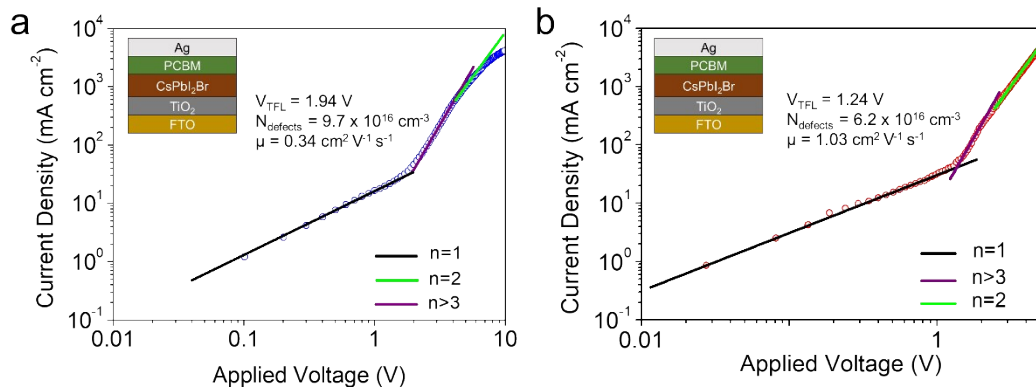


Figure S14. SCLC measurements of electron-only devices of (a) control and (b) HSW CsPbI₂Br film. Inset is the device structure for SCLC test.

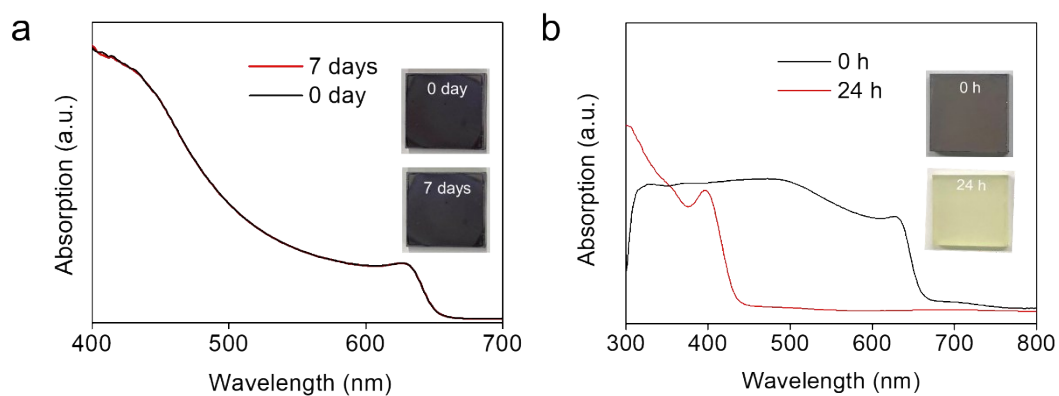


Figure S15. (a) UV-vis spectra of HSW CsPbI₂Br films after exposure to dry air for 7 days. The relative humidity is $15 \pm 3\%$. (b) UV-vis spectra of the control CsPbI₂Br films after exposure to dry air for 24 h. Insets are photographs of corresponding films.

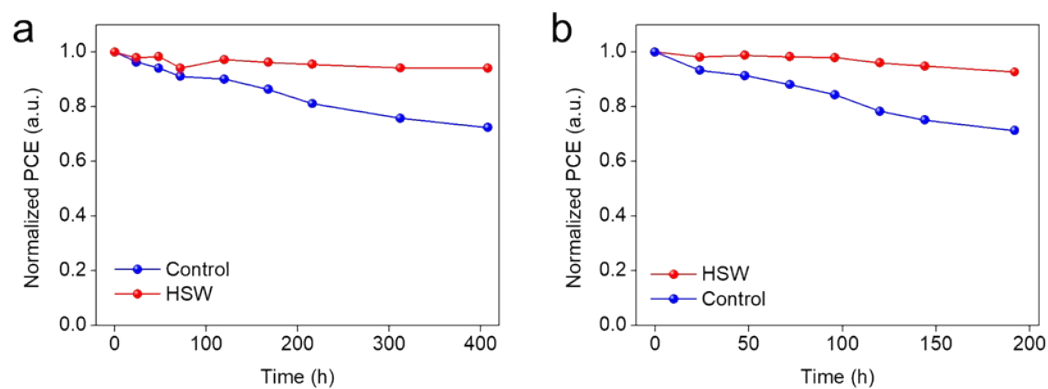


Figure S16. (a) Operational stability measurements of control and HSW CsPbI₂Br devices under continuous one-sun illumination (100 mWcm⁻²) in N₂-filled glovebox. (b) Thermal stability measurements of control and HSW CsPbI₂Br devices heated to 85 °C in N₂-filled glovebox.

Table S1. Carrier lifetimes of CsPbI₂Br films obtained by fitting TRPL spectra.

Samples	τ_1 (ns)	τ_2 (ns)
Control	0.86	3.74
HSW	6.73	30.05

Table S2. Photovoltaic parameters of champion CsPbI₂Br solar cells prepared with different concentration of H₂O.

H₂O/IPA	J_{sc} (mA cm⁻²)	V_{oc} (V)	FF	PCE (%)
0%	7.77	0.52	0.38	1.52%
0.5%	10.60	0.90	0.52	4.94%
1.5%	15.98	1.33	0.78	16.47%
3%	15.25	1.22	0.74	13.77%
5%	14.46	1.06	0.68	10.47%

Table S3. Photovoltaic parameters of champion HSW CsPbI₂Br solar cell with different scan directions.

	J_{sc} (mA cm⁻²)	V_{oc} (V)	FF	PCE (%)
Reverse	15.98	1.33	0.78	16.47%
Forward	15.86	1.31	0.77	16.15%

Table S4. Comparison of the photovoltaic parameters of some reported CsPbI₂Br solar cells.

J_{sc} (mA cm⁻²)	V_{oc} (V)	FF	PCE (%)	Ref
15.98	1.33	0.78	16.47	This work
16.95	1.18	0.80	16.15	1
16.82	1.15	0.75	14.69	2
15.8	1.18	0.72	13.6	3
15.45	1.21	0.79	14.85	4
15.86	1.32	0.75	15.50	5
15.28	1.30	0.78	15.56	6
15.1	1.15	0.78	13.57	7
14.65	1.22	0.81	14.65	8
15.3	1.30	0.81	16.2	9

Reference

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